THE ANALYST.

OCTOBER, 1893.

THE LATE MR. C. W. HEATON, F.I.C., F.C.S.

It is with much regret that we chronicle the death, at the age of 58, of Mr. C. W. Heaton, the treasurer for many years past of the Society of Public Analysts. Mr. Heaton was best known as Professor of Chemistry in the Medical School of Charing Cross Hospital, a post which he filled from the year 1862 until the time of his decease. He also held the post of Examiner in Chemistry to the Royal College of Physicians and the Royal College of Veterinary Surgeons, and was Public Analyst to the parish of St. Martin-in-the-Fields. His chief work in applied chemistry was connected with the subject of coal-gas and its purification, also with the recovery of sulphur from waste products; but he directed no inconsiderable attention to the subject of food analysis, and contributed various papers to the pages of The Analyst. As a pupil of the late Mr. Dugald Campbell, and subsequently as an assistant to the late Dr. Stenhouse, Mr. Heaton was one of the best-known links between the earlier and later generations of consulting chemists, and his friendships in the profession were many and far-extending. His loss will be mourned not merely among his colleagues in the Society, but in the whole circle of chemical life throughout this country.

ON SOME MODIFICATIONS IN THE BABCOCK MACHINE.

By Chas. R. C. Tichborne, LL.D., F.I.C., D.P.H., etc.

(*Read at the Meeting, July 18th*, 1893.)

Although a great deal has been written upon the value of the Babcock, Leffmann-Beam, and Lactocrite machines, perhaps I shall be excused if I say a few words as regards my own experience of the results obtained with the Babcock, as specially contrasted with the ordinary ether analysis. This experience has been gained after some thousands of estimations.

I may sum up my opinion of the proper place of the Babcock as only being a valuable adjunct to a busy laboratory, and to be worked under the supervision of a trained expert. The working of such machines by a trained hand is a very important element of success. I say this advisedly, because many of the Dairy Co-operative Societies with whom I am connected fail to get the value out of machines like the Lactocrite or Babcock.

My observations and experience confirms what has already, in many cases, been ably pointed out by members of the Society of Public Analysts, but as some of them are not quite agreed, I will enumerate my own conclusions without going into details.

1. Any machine working by centrifugal force for the separation of butter fat is largely dependent upon the mechanical condition of the fluids, and is liable to hidden errors. It therefore should never be used by the Public Analyst for prosecuting purposes.

2. If the separated butter line is clear from curd and above the average, it may be looked upon as a reliable assay. If anything below 3 per cent., it should be looked upon with caution, and centrifugal instruments are unreliable for milk containing less than 2 per cent. of butter-fat.

"Why do I select the Babcock machine?" is a question which has been partially answered by others, notably Mr. Embrey. My chief object is to work with an apparatus which gives me butter-fat alone, without the use of such objectionable adjuncts as fusel-oil. Again, the high speed required in the other instruments is a very serious objection when they are in constant use.

It has been pointed out that a correction is required, which Mr. Embrey views as a constant quantity, and fixes at 0·3. I have come to the same conclusion as regards a correction being necessary, but my experience does not lead me to think it is a constant quantity, but that it must be changed according to the richness of the milk in the machine, *i.e.*, that the correction for milk under 2 per cent. of butter-fat will be slightly different from that about 3 per cent. I should mention that according to the modification I am about to detail in the machine, the reading of the butter lines is conducted at a much more uniform temperature than was the case with the old machine.* The fact probably enables one to watch the question more effectively.

The strength of the acid, as shown by previous observers, is of great importance, and the success of the estimations mainly depends upon this point: either too strong or too weak is equally objectionable.

In the old machine we were directed to put hot water into the tank. The following are the directions:

"As soon as the bottles have been sufficiently whirled they should be filled to the neck with hot water. The cover should then be replaced and the machine turned for one or two minutes, after which more hot water is added, filling the tube to about the 7 per cent. mark.

"The fat will slowly rise into the graduated tube, losing its cloudy appearance as it passes through the hot water. When all the bottles are filled the cover is put upon the tank and the machine again turned for a short time.

"During this time the water in the tank should be kept hot by pouring in a quantity of boiling hot water before starting the machine. If the fat in some of the tubes still has a cloudy appearance, the cover should be placed upon the tank and more boiling water added for a few minutes, when the fat should become clear and in condition to be measured. The clearing may be hastened by whirling the tubes while hot.

"The fat when measured should be warm enough to flow readily, so that the line between the acid liquid and the butter-fat will quickly assume the horizontal position

* As every operator has his own method of working, and as the machines may differ to some slight extent, I have thought it better not to give any arbitrary correction. As a matter of fact my experience points to an addition of 0·3 to quantities less than 2 per cent., 0·2 on 2·5 per cent., and 0·1 or 0·0 above this percentage.

when the bottle is removed from the machine. Any temperature between 110° F. and 150° F. will answer, but the *higher* temperature is to be preferred.

"The slight difference in the volume of fat due to this difference in temperature is not sufficient to materially affect results. A difference in temperature of 40° F. will make less than $\frac{1}{10}$th per cent. difference in milk containing 5 per cent. of fat."

It will be seen that this process entailed a considerable amount of work to get a nice clear separation, and it is only in the summer that we can work with any degree of certainty, commensurate with quickness, and the value of the machine is entirely dependent upon the perfect separation of the fat in a clear condition. This clouding of the fat is most objectionable in the winter time with a laboratory at a temperature of 50° F The "hot water" was chilled on the first two or three revolutions; the revolving case was simply blowing cold air across the *graduated stem*, this being the part of all others which required to be in a perfectly warm and uniform condition, so that the fat should remain permanently liquid during the whirling of the bottles. This is remedied in the new form of Babcock by putting a pint of boiling water into the lid of the chamber, which is made hollow for the purpose. The heat is thus applied to the stem, not to the body of the bottles. Any cool air that is whirled in strikes upon the hot lid and is whirled across the thin stems.

The old and present machines are provided with a case or chamber, in which the bottle charged with milk and acid are put, in sockets arranged round the chamber. The narrow, elongated stems, in which the butter-fat collects after whirling, and is measured, are placed close to the lid of the chamber, like the spokes of a wheel. In the old machine this is simply a tin cover. In the new machine it is a chamber about an inch deep and covering the whole top of the machine. It is, of course, removable for the purpose of getting out the bottles. At the apex there is a little funnel, through which a pint of water at 212° F. is introduced.

Now, it must not be forgotten that the final separation between the butter-fat and the acid and insoluble nitrogenous matter takes place in the stems and not in the bodies of the bottles, and thus the importance of keeping these parts of the apparatus above the melting-point of butter-fat.

The following is the result of comparative working of the instruments:

	New Machine.	Old Machine.
1.	2·3 ...	2·2
2.	3·6 ...	3·5
3.	3·2 ...	3·0

The great saving, however, is in time, the operation being perfectly completed in two terms of five minutes duration each. A quantity (say a pint) of boiling water having been placed in the lid, the assay is effected at a uniform temperature, which is of considerable importance where the milk is rich in butter-fat, as the error due to contraction or expansion is exaggerated. The expansion is stated in the original to make no difference. This is not correct. I find that it holds good for 2 per cent. of fat, but that if there is 3 or 4 per cent. of butter-fat this error becomes much more important. With the same ratios it would read that the difference of temperature which makes 2 per cent. of fat read $2\frac{1}{10}$ per cent., would in the case of 4 per cent. of fat make an error of 0·2 per cent., or the 4 per cent. would read 4·2 per cent.

Mr. Lister, whose machines are described in the May number of The Analyst, has adopted our lid on his machines. I may as well state that the form of machine before you has been protected by myself and Mr. Thompson, of Messrs. Carson and Sons, Dublin, who made the first one at my suggestion.

VINEGAR.

By A. H. Allen and C. G. Moor.

(*Read at the Dublin Meeting, July 18th*, 1893.)

Recent events, well known to the members of this society, have compelled public analysts to give more attention to the chemistry and manufacture of vinegar than the majority of them had previously done. In a recent number of The Analyst there appeared an abstract of a paper by us in which we gave a number of definitions of "vinegar" which we had collated from various sources. Some of these definitions were not drawn by their authors with the expectation of their being quoted in judicial proceedings, and are not unnaturally wanting in the requisite precision on the one hand and the necessary elasticity on the other. Before making an attempt ourselves to formulate a more satisfactory definition of "vinegar," we propose to review shortly the chief processes by which the various products commercially posing as vinegar are manufactured.

No naturalist has any difficulty in classifying a *cow* as an animal and a *cabbage* as a vegetable; but in the case of some of the lower forms of life the biologist is at a loss how to regard the specimen. So it is with vinegar, some commercial products almost defying classification.

The so-called vinegars of commerce may be broadly divided into two classes: those which are the product of the consecutive alcoholic and acetous fermentations, and those which are not. The view is pretty general amongst public analysts that products of the former class have alone the right to be called "vinegar," unless some adjectival prefix be used, such as "wood-vinegar."

Of course the original vinegar was made from wine, as the derivation of the word shows; but in this country wine-vinegar has been almost wholly superseded by malt-vinegar. This again has been superseded, so far as a product made from malt only is concerned; for, just as the beer-brewer has discovered that the substitution of unmalted barley for a portion of the malt is distinctly advantageous, so the vinegar-brewer invariably uses more or less unmalted grain in admixture with the malt. But the beer-brewer has, since the abolition of the duty on malt, largely replaced the malted and unmalted barley by maize and rice, or the "glucose" prepared therefrom by the action of dilute acid; and the vinegar-manufacturer has not been slow to follow suit, and to use sugar and molasses in addition. So general has this practice become that the vinegar-manufacturers who still brew from malted and unmalted barley only might be counted on the fingers of one hand (without reckoning the thumb). Under these circumstances, it is evident that the term "malt-vinegar" is a misnomer, and it behoves public analysts to consider how far they will be justified in permitting the sale of products of mixed origin under the title of "malt-vinegar." There is undoubtedly a popular preference for, or prejudice in favour of,

malt-vinegar; but while manufacturers are quite ready to pander to this preference, whether it be justified or not, they do not always supply an article to which the name "malt-vinegar" can be properly applied, even when used in the extended sense of a product brewed from a mixture of malted and unmalted grain. The contention that by such a term a vinegar merely *flavoured* with malt is to be understood will scarcely bear investigation. Take the case of jam. Are we to understand by "raspberry-jam" an article composed chiefly of apples or turnips, and containing only enough raspberry to give it the characteristic flavour? Or under the title of "malt-whisky" are we to admit a spirit made not only from unmalted barley, but also from rice, maize, dari, potatoes, sugar, molasses, etc.? It would undoubtedly prevent much heartburning, and greatly simplify the question at issue, if the term "malt-vinegar" were definitely abolished.

But the substitution of other fermentable materials for barley is not the only trade-practice the legitimacy of which calls for consideration. The albuminoids present in malt-wort and other vegetable infusions have a prejudicial effect on the keeping properties of the vinegar produced therefrom, especially in the case of the weaker qualities, and it is the object of the scientific vinegar-manufacturer to reduce these to a minimum. Hence it is the practice of some manufacturers to distil a portion of their product—which, contrary to the general impression, can be done very cheaply—reserve the stronger portion of the distillate for sale as "distilled vinegar," and add the weaker fractions to some of the undistilled article. Distilled malt-vinegar is not, as is sometimes erroneously assumed, merely dilute acetic acid. On the contrary, it contains quite appreciable quantities of alcohol, acetal, acetic ether (and probably other esters), furfurol, aldehyde, etc.; and has a highly characteristic taste and odour which appear to be greatly appreciated in Scotland, where distilled vinegar is seen more frequently than the coloured article.

We have obtained the following figures by the analysis of distilled *vinegar* (not mere acetic acid) manufactured by some of the leading vinegar-brewers:

	A.	B.	C.
Specific gravity	1·0077	1·0080	1·0055
Acetic Acid (grammes per 100 c.c.)	5·16	5·80	3·88
Total solids ,, ,,	0·006	0·013	0·032
Ash ,, ,,	None.	None.	None.

It is evident that the addition of either of the above distilled vinegars to an undistilled product would tend to alter materially the proportions of certain of the constituents of most value to the analyst in judging of the origin and mode of manufacture of a sample of vinegar. In fact, the manufacturer who practises the addition of a distilled vinegar to his undistilled product runs considerable risk of having his article certified to contain added acetic acid.

Two samples of still-residues from the manufacture of distilled vinegar have been examined by us. They were brown, and of the consistence of treacle. On analysis they yielded the following figures:

	A.		B	
Total solids	43·20	per cent.	72·30	per cent.
Ash	8·38	,,	9·21	,,
Alkalinity of Ash (K_2O)	2·07	,,	1·40	,,
Phosphoric Acid	2·67	,,	0·24	,,
Nitrogen	2·63	,,	2·63	,,

A was a residue from a true barley vinegar. B was derived from a vinegar brewed with a considerable proportion of rice.

Under the name of "Essig Sprit," or "spirit-vinegar," there is now sold considerable quantities of an article of foreign origin, which is manufactured by subjecting previously distilled potato-spirit to the acetous fermentation. The product has many of the characters of English brewed vinegar, and of course contains those peculiar secondary products of the growth of *Mycoderma aceti* which give vinegar certain of its valued characters. It is usual to add a certain proportion of malt-wort to the spirit, or of malt-vinegar to the fermented product. *Essig Sprit*, as imported, contains about 13 per cent. of acetic acid, and a notable proportion of acetic ether; but the colouring matter is added in England, whereby the article is imported as "acetic acid," and escapes the duty payable on "vinegar." The following figures show the composition of "Essig Sprit" in its concentrated form, and of the "spirit vinegar" of commerce obtained by diluting and colouring it:

Grammes per 100 c.c.	Essig Sprit.	"Vinegar."			
		A.	B.	C.	D.
Specific gravity ...	1·0152	1·0095	1·0086	1·0068	1·0096
Acetic acid	11·26	4·68	4·50	3·75	4·80
Total solids... ...	·64	0·79	0·50	0·40	0·65
Ash	·06	0·04	0·05	0·03	0·06
Alkalinity of ash ...	—	Trace	Trace	Trace	0·01
Phosphoric acid ...	Trace	0·002	None	None	Trace
Nitrogen	0·014	0·0084	0·0098	0·0110	0·013
= Albuminoids	0·089	0·053	0·062	0·069	0·082

Another product of German manufacture, which finds its way into English commerce to a considerable extent, is prepared by fermenting potato-spirit with *Mycoderma aceti*, neutralising the dilute acetic acid so obtained with "pure lime," and distilling the resultant calcium acetate with an acid. Another manufacturer neutralises the acid with soda instead of lime. By this means a very concentrated acetic acid is obtainable, the strength of which ranges from 40 to close upon 90 per cent. When suitably coloured and flavoured, such acid is extensively sold under such names as "malt acid," "vinegar essence," "vinegar extract," etc., from which a factitious vinegar can be prepared by simple dilution with water. The following figures were obtained by us some time since by the analysis of samples of this so-called "malt acid" and the "vinegar" obtained by its dilution.

Grammes per 100 c.c.	"Malt Acid."		"Vinegar."	
Specific gravity	1·0825	1·0977	1·0191	1·0125
Acetic acid	88·02	45·4	3·84	8·11 (*sic*)
Total solids	2·77	12·14	2·00	0·27
Phosphoric acid (P_2O_5) ...	—	0·017	Present.	—
Ash	0·15	0·180	0·04	—
Nitrogen	—	0·113	—	—
= Albuminoids	—	0·70	—	—
Sulphuric acid (free) ...	—	0·74	0·063	—

The production of a liquid containing more than 14 to 15 per cent. of acetic acid by the acetous fermentation is simply impossible, and the practical limit is reached in Essig Sprit with about 13 per cent. But vinegar-brewers do not, as a rule, aim at producing an article containing more than 6 per cent. at the outside. Hence the mere fact of a liquid having an acidity corresponding to 80 or even to 40 per cent. of acetic acid is absolute proof that it is not a product of fermentation, whatever the manufacturer may declare. Nor can a vinegar resulting from fermentation be, in practice, materially concentrated by evaporation, although absolute acetic acid has a boiling-point somewhat above that of water. Thus, on distilling a sample of commercial malt vinegar, containing 4·17 grammes of acetic acid per 100 c.c. to half its bulk, we found the distillate to contain 2·87 grammes of acetic acid per 100 c.c., while the liquid remaining in the retort contained 4·38 per 100 c.c. On reducing 500 c.c. of the same vinegar to 15 c.c. by distillation, without the use of any fractionating arrangement, the residual liquid contained only 10·1 per cent. of acetic acid. A similar experiment made on a mixture of malt vinegar and acetic acid B. P., containing before distillation 14·16 grammes of $C_2H_4O_2$ per 100 c.c., yielded a distillate containing 10·92 of acetic acid, while the half remaining in the retort retained 17·4 grammes of acid per 100 c.c.

We have recently met with as many as ten samples of vinegar containing a notable quantity of free sulphuric acid, though it is right to add that there is reason to believe these were all supplied to the retailers by the same "vinegar maker." This article was stated to be made by adding to the vinegar brewed from 2 cwt. of malt and 1 cwt. of molasses 25 gallons of "wood-vinegar," and sufficient water to reduce the strength of the mixture to a little over 4 per cent. of acetic acid. From these data we calculate that the product would contain about 8 per cent of true fermentation-vinegar. On analysis it has given the following figures :

	Specific gravity	1·0130 to 1·0138
Grammes per 100 c.c.	Acetic acid	4·0 ,, 4·2
	Total solids	1·6 ,, 1·7
	Ash	0·06 ,, 0·09
	Phosphoric acid	Trace.
	Sulphuric acid (free)	0·22 ,, 0·30
	Nitrogen	0·016 ,, 0·020

The residues obtained by the evaporation of these vinegars were quite black.

The solicitor who defended the vendors of this article, the casks containing which were labelled by the manufacturer "pure malt vinegar," stated that its manufacture cost as much as true malt vinegar. Taking the price of 25 per cent. acetic acid at 7s. per cwt. (as per list in the *Chemical Trade Journal*), it follows that a 4 per cent. "vinegar" could be made therefrom for a trifle over 1½d. per gallon.

We have tried to compare the taste of dilute acetic acid with that of sulphuric acid, and find the latter to leave a sourness on the palate equal to an acetic acid of fully four times the strength. Hence 0·25 per cent. of sulphuric acid is palatably equivalent to about 1·0 per cent. of acetic acid, and the manufacturer who adds it can reduce his bill for the latter by 25 per cent. Arsenic-free sulphuric acid of 1·725 specific gravity is quoted at 26s. per ton; whence it follows that a dilute acid

equal in sour taste to a vinegar containing 4 per cent. of acetic acid can be manufactured for 2d. per 100 gallons !

We may here express our opinion that the use of the term "pyroligneous acid," to express the quality of wood acetic acid used in the production of factitious vinegar, is misleading. By pyroligneous acid is commonly understood an acid obtained by the distillation of wood. By conversion into a calcium or sodium salt it can be readily purified to a much greater extent than if neutralization be omitted, and when recovered from its salt by distillation with a mineral acid it is technically known as "acetic acid." Although the term pyroligneous acid is very convenient for indicating the origin of an acetic acid, it implies the presence of tarry matters, which, in our experience, do not exist in the acetic acid employed for manufacturing factitious vinegar.

In order to obtain more reliable information respecting the composition and range of variation of vinegar prepared from different materials, we have obtained samples of representative vinegars from most of the leading vinegar-brewers, and have analysed these samples in some detail. The actual figures obtained we reserve for the present. Our analyses have included the determination of specific gravity, total acid in terms of acetic acid, total solids, ash, the alkalinity of the ash in terms of K_2O, the phosphoric acid, the nitrogen by Kjeldahl's process, free sulphuric acid when present, tests for heavy metals, and qualitative tests for alcohol, furfurol, aldehyde, acetic ether, etc.

With regard to phosphoric acid, the importance of which as an indication of the origin of vinegar was pointed out in "Commercial Organic Analysis," vol. i., p. 389, and has since been insisted on by Hehner (ANALYST, xvi., 81), its value as a quantitative method is seriously discounted by the influence on the composition of the wort produced by the use of hard water. As, however, any precipitation of phosphate of calcium thus occasioned is more than counterbalanced by the formation of a corresponding soluble salt, the proportion of total ash is not reduced thereby.

The "alkalinity" of the ash when obtained is also a useful indication, but we have not found the results very concordant. A better plan is undoubtedly to determine the actual potash, as is practised by R. R. Tatlock. It is very difficult to obtain a fairly white ash by the combustion of vinegar-residues, and if the temperature be too high, or the ignition very prolonged, there is a serious danger of losing some of the more volatile salts. In our later experiments, therefore, we have adopted the practice of sulphating the ash. This does not interfere with the determination of potassium by direct precipitation with platinic chloride in the portion of the ash soluble in water. In practice we find it convenient to take 5 c.c. for the determination of the extract, and having weighed the total solids, to add another 20 c.c. of the same vinegar, and again evaporate. When reduced to the consistency of a syrup, a few drops of strong sulphuric acid are added, the evaporation completed, and the residue ignited at a low red heat. By these means a perfectly white and practically infusible ash is readily obtained. As a rule, 115 to 120 parts of the sulphated ash represent 100 parts of unsulphated ash, the extreme limits hitherto observed being 106 and 130. Of course the ratio will vary with the composition of the ash, and

consequently with the origin of the vinegar, and may in the future afford very valuable information.

With regard to the determination of nitrogen, we find it convenient to operate on 20 c.c. of the vinegar, though a smaller quantity will suffice. When concentrated to a syrup, we employ Gunning's modification of the Kjeldahl process. We have also obtained very good results by Stock's oxide of manganese process.

For the determination of free acetic acid in vinegar we employ 10 or 20 c.c. of the sample, which we titrate in a weighed porcelain dish with caustic soda, using phenol-phthalein as an indicator. There is not the least difficulty in noting the end of the reaction, without diluting the vinegar or taking any other precaution. The neutralized liquid is distilled, and the distillate tested for the volatile constituents of vinegar. Alcohol is readily recognised by the iodoform test, and aldehyde by the rosaniline sulphite reaction. Acetic ether can be determined by Berthelot's method, similar to Koettstorfer's process for oils. Furfurol, we at first thought might be indicative of acetic acid derived from wood, especially as the ordinary acetic acid of commerce gives abundant evidence of the presence of furfurol when tested by the aniline acetate reagent. Unfortunately there is either furfurol or a body giving a similar reaction produced when sugar is caramelised. On treating the resulting caramel with water, distilling, and testing the distillate with the aniline acetate reagent, a strong furfurol reaction is obtained.

We have attempted to find some compound which would be directly indicative of a brewed vinegar as distinguished from the various forms of distilled acetic acid. Alcohol is only practically valuable for this purpose in special cases, and the objections to relying implicitly on the natural presumption from its presence are obvious. Glycerin, another constant product of the alcoholic fermentation, is very difficult to determine in the presence of some of the other constituents of vinegar. We have attempted, therefore, to determine the succinic acid, which substance the experiments of Pasteur showed to be a constant product of the alcoholic fermentation. There are great difficulties in its accurate determination under the conditions with which analysts have to deal in practice, but our experiments in this direction are not complete, and we are not hopeless that we may be able to devise a practicable method of dealing with it.

In interpreting the results obtained by the analysis of vinegar, it is important to eliminate the variations due to differences of dilution. This may be effected to some extent by expressing all the items per 100 parts of acetic acid, but a far preferable plan is to adopt the principle suggested by Hehner (ANALYST, xvi., 82), who calculates the amount of phosphoric acid, ash, etc., per 100 parts of the original solids of the vinegar. These are deduced from the fact that 180 parts of glucose yield theoretically 120 parts (or two-thirds of its weight) of acetic acid. Hence, by multiplying the acetic acid found in the vinegar by 1·5, and adding to the product the percentage of total solids still existing in the vinegar, the "original solids" are obtained. In practice, the actual yield of acetic acid is rarely more than two-thirds of the theoretical amount, so that a more accurate expression of the original solids of the wort would be obtained by multiplying the percentage of acetic acid by 9/4 (= 2·25), and adding the extract to the product.

We purposely leave any discussion of the deductions from the foregoing analytical data for the present, as also the actual figures we have obtained by the analysis of the numerous samples of typical vinegar, with which we have been kindly furnished by a number of the leading vinegar-brewers of the kingdom. We may, however, conveniently give here the results of the analysis of two special vinegars. One of these was manufactured on the large scale from locust-beans; the other was a domestic product, obtained simply by fermenting a solution of brown sugar with brewers' yeast, and allowing the liquid to stand in a loosely-covered vessel:

		Locust-bean Vinegar.	Sugar Vinegar.
	Specific gravity ...	1.0217 ...	1·0284
Grammes per 100 c.c.	Acetic acid	7.26 ...	6·90
	Total solids	2.47 ...	4·69
	Ash	0.31 ...	0·46
	Alkalinity (K_2O) ...	0.11 ...	—
	Phosphoric acid ...	trace ...	trace
	Nitrogen	0·03 ...	0·046
	= Albuminoids ...	0·189 ...	2·290

SOMERSET HOUSE AND WATER ANALYSIS.

By F. W. Stoddart.

The following notes may be of interest, as throwing some light upon the views entertained by the Somerset House chemists upon this very important subject.

The water of a shallow well supplying a poor district in Bristol was found to yield very marked evidence of sewage pollution of the "oxidized" type common in similar situations, and action was taken by the Sanitary Authority to close the well. Analyses put forward on behalf of the owners of the property agreed fairly in all respects with my own, except that nitrates were confessedly ignored as being of no importance; and, following the lines of a well-known text-book, the water was described as of excellent quality.

In view of considerable opposition, an independent opinion was considered advisable, and Mr. Hehner was requested to report on the water. His figures are included in the annexed table, and his opinion, based on those figures, coincided with that I have already expressed, viz., that the water was polluted with sewage, and dangerous to health.

The well in question is situated at the foot of a millstone grit hill, composed of beds of rock of the usual character, dipping sharply at an angle of about 25°. It is sunk entirely in this formation, is 45 feet deep, and is not puddled, but built round with loose stone, uncemented. It is immediately surrounded by a nest of houses of a poor class, and is, indeed, placed beneath a small paved yard attached to one of the houses, the other end of the yard being occupied by a privy. Numerous drains, some of which have recently been defective, are known to exist within a few feet of the well, and there is an old graveyard at a distance of a few yards. The steep slope of the hill, and the whole of the table land at its summit, are thickly inhabited, forming, indeed, a great part of Clifton; so that there is no possible gathering ground of a satisfactory description.

The natural unpolluted water from this formation almost always yields less than 0·1 grain per gallon of nitrogen as nitrates, with total solids ranging from 20 to 30 grains. The chlorine is variable according to the position, but samples from the immediate neighbourhood have contained 1 to 1·5 grains.

The hearing of the case was very prolonged, and ultimately the bench decided to refer the matter to Somerset House. A sample was sent on June 4, and after a fortnight's delay a series of questions as to the circumstances of the well was received; as the replies were necessarily in every instance unfavourable to the water, it was naturally supposed that any doubts as to its polluted character would be dispelled.

No report, however, was forthcoming, and only after repeated applications for some expression of opinion was a letter received containing a proposal that the matter should *stand over until November.*

As the local Authority was intent on setting its house in order in view of a possible cholera invasion, and as the evidence of pollution was quite conclusive, this proposal was naturally declined; and finally, after further pressing, the following report, dated July 25, was received on August 9, a period of more than two months having elapsed since the sample was despatched. It will be noted that Dr. Bell's name, which headed the list of signatures in the previous correspondence, does not appear in connection with the report, the figures of which are included for convenience in the table.

"Laboratory, Somerset House, W.C.

"Judging from the figures shown under the terms 'albuminoid ammonia' and 'oxygen absorbed,' the water is regarded as of moderately good quality, and affords no evidence of serious contamination with organic impurities. The proportion of nitrates is high, but they are not in themselves injurious, and do not necessarily indicate that the water has been exposed to recent sewage contamination. There are good grounds for believing, from the character and amount of the chief mineral matters contained in the water, that the great bulk of the water is derived from a deep or distant source, and that the well is not dependent for supplies from the soil of the immediate neighbourhood; for it would be reasonable to expect more definite evidence of present sewage contamination if leakage took place from the drain-pipes which lie—it must be admitted—in almost dangerous proximity to the well.

"Although this water is unsatisfactory in some respects, and we should not recommend it, we do not feel justified from a consideration of the results of the analysis in giving an opinion that the use of the water for potable purposes would be dangerous to health.

"As witness our hands this 25th day of July, 1893.

"(Signed) R. Bannister, F.I.C., F.C.S.
G. Lewin, F.I.C."

Little comment is needed on my part. The undecided tone unfortunately characteristic of certificates from the same source is here displayed to perfection.

The suggestion that, because in the opinion of Messrs. Bannister and Lewin the water is not wholly supplied from the polluted subsoil, it is therefore fit for drinking is, perhaps, especially worthy of note.

It is, however, simply lamentable that this water, a typical example of the class most insidiously dangerous, because inoffensive or even attractive to the unaided senses, should be described as safe by an official department naturally of importance in the eyes of the general public, thereby raising a serious obstacle to the most important of all sanitary improvements.

There are large numbers of shallow wells in Bristol, and probably in many other large towns, supplied more or less completely from a subsoil of the filthiest description, which furnish water of this character; and this applies especially to those districts in which the cholera raged most furiously in previous epidemics.

There is, of course, no necessity whatever to make Somerset House a court of reference in matters relating to water supplies, and I imagine no public health officer acquainted with the details of this case will consent to such a procedure in future.

	May 18.	May 20.	June 4.
	Stoddart.	Hehner.	Somerset House.
Saline ammonia	0·0017	0·0008	0·002
Albuminoid ammonia ...	0·003	0·0022	0·0047
Nitrogen as nitrates	1·79	1·81	2·44
Chlorine	3·70	3·71	3·58
Oxygen absorbed 15 min. ...	0·018	0·015	——
,, ,, 4 hrs. ...	0·025	0·043	0·026 (3 hrs.)
Total dissolved solids ...	53·0	53·6	55·5
Phosphoric acid	Strong trace	Very heavy trace	——
Sulphuric acid	——	7·92	——
Loss on ignition	——	6·16	——
Total hardness	36·0	——	28·1
Permanent do.	21·0	——	——

All results in grains per gallon.

Sheep's Milk and the Manufacture of Cheese therefrom. C. Besana. (*Staz. Sper. Ag. Ital.*, xxiii. 572.)—The author has made a study of the milk of the sheep and the products derived therefrom, a research undertaken at the instance of the Minister of Agriculture. Some preliminary results have already been published in the *Bolletino di notizie agrarie*, 1887, 57; 1890, 26; and 1891, 18. Much of this important memoir is not suitable for an analytical journal, but the following portions will be of interest to analysts:

The Milk of the Sheep.—A sheep under ordinary circumstances has been found by the author to yield 45 to 50 litres of milk per annum; Pouriau has found with the Roquefort flock 55 litres a year (*La Laiterie*, 1881, 12), and Fleischmann gives as limits 25 to 140 litres (*Das Molkereiweisen*, 1876, 88); he quotes some Dutch sheep which gave 500 (?) litres a year. This quantity varies greatly in individuals,

and according to the season; thus, with three sheep kept for special observation, the following mean daily quantities were found:

	Litres per Day.	Meals counted and measured.
No. 1	0·374	41
,, 2	0·552	35
,, 3	0·275	15

In his observations at Prima Porta in 1891, after a prolonged drought, the author found that 1,000 sheep gave 66 litres per meal, as against 150 and 130 litres per meal found in former years after normal seasons; the richness of the milk was also much less in 1891 (*see post*).

Density of the Milk.—The density of the milk of the three sheep mentioned varied from 1·037 to 1·043, with an average of 1·0395 (176 observations). The variations of the mixed milk of a flock were 1·035 to 1·039; Fleischmann (*loc. cit.*) gives 1·035 to 1·041 as the limits.

Influence of Temperature on the Density of Sheep's Milk.—The author has calculated a table for correcting the densities of sheep's milk for temperature:

Temperature.	Difference in Degrees for 1 Degree Cent.	Correction.
5° to 10°	0·20	Subtract 1·25 and 0·20 for 1 degree under 10°.
11° to 15°	0·25	Subtract 0·25 for each degree under 15°.
16° to 20°	0·30	Add 0·30 for each degree over 15°.
21° to 25°	0·32	Add 1·5 and 0·32 for each degree over 20°.
26° to 30°	0·35	Add 3·1 and 0·35 for each degree over 25°.
31° to 35°	0·37	Add 4·85 and 0·37 for each degree over 30°.
36° to 40°	0·40	Add 6·7 and 0·40 for each degree over 35°.

Effect of Watering on the Density.—The mixed milk of two sheep was diluted with varying amounts of water:

Sample.	Density.	Diminution.	Diminution for each 10%.
Genuine	39	—	—
5%	37	2	—
10%	35½	3½	3½
20%	32½	6½	3
30%	30	9	2½
40%	28	11	2
50%	26	13	2

Fat Globules.—The microscopic appearance of sheep's milk is like that of the cow; the globules are, however, larger in size. The author found the globules of cow's milk to vary from 0·0016 mm. to 0·0100 mm., and of sheep's milk from 0·0047 mm. to 0·0309 m.m. This character may be of service in cases of adulteration of cow's milk with sheep's milk.

Creamometry.—Sheep's milk throws up no cream in 48 hours, owing to its great density and viscosity; if diluted with an equal bulk of water, 14 per cent. of cream was thrown up in 24 hours and 20 per cent. in 48 hours; after 48 hours the cream-layer did not increase.

Chemical Composition.—The analysis of eight samples are given:

A. Milk of a flock of 2,700 sheep at Santa Maria di Galera, 1887, evening.
B. *Ibid.*, morning.
C. Milk of a flock of 2,500 at same place, 1890, evening.
D. *Ibid.*, morning.
E. Milk of a flock of 2,498 at Prima Porta, 1891, evening.
F. *Ibid.*, morning. There had been a very bad season this year, and the yield was very low (*see ante*).
G. Milk of a flock of 2,000 at Rome, 1892, morning.
H. Milk of three sheep kept for experiments at Lodi, 1892, morning.

	A.	B.	C.	D.	E.	F.	G.	H.
Water ...	78·37	79·04	77·27	77·92	80·15	80·83	78·56	78·37
Fat	8·99	8·90	10·38	10·04	7·25	7·12	9·41	9·30
Proteids ...	6·55	6·10	6·28	6·22	6·03	5·84	6·14	6·20
Sugar ...	5·08	5·04	4·98	4·93	5·20	5·20	4·93	4·99
Ash	1·01	0·99	1·09	0·89	1·37	1·01	0·98	1·09
Total ...	100·03	100·13	100·00	100·00	100·00	100·00	99 96	100·02
Density ...	1·0381	1·0374	1·0381	1·0379	1·0375	1·0373	1·0362	1·0391

The author prefers to neglect Samples E and F in calculating the mean composition, as they are undoubtedly abnormal; the mean composition of the others is:

Water...	78·23
Fat	9·50
Proteids	6·26
Sugar	5·00
Ash	1·01
Total	100·00
Density	1·0378

The most important difference between this milk and cow's milk is the large amount of fat in sheep's milk—about two and a half times that in the milk of the cow; the amount of proteids is also much greater.

The extraordinary richness in fat gives this milk a greasy feeling when touched, a character also possessed by all its products; when the milk is warmed to the temperatures employed in cheese-making, oily drops separate.

Determination of Fat.—The author finds that the use of Marchand's lacto-butyrometer gives results sufficiently exact for practical dairy work; he finds it necessary to dilute the milk with an equal volume of water and to add a few drops of ammonia. It is advisable to make three experiments, using respectively two, three, and four drops of ammonia, and to take the highest result as the correct one. In the whey obtained from sheep's milk the fat can be directly estimated by this method.

Spontaneous Acidification.—Sheep's milk takes about twice as long to curdle spontaneously as cow's milk. The author does not attribute this wholly to differences in composition, but thinks that as the sheep were kept in the open country, while the cows live in sheds, the sanitary conditions are more favourable in the case of the sheep. This character is, however, very precious for cheese-making.

Action of Rennet.—The curd yielded by sheep's milk is dense, homogeneous and firmer than that yielded by cow's milk. The milk of the sheep requires about double the quantity of rennet necessary for that of the cow. This holds good whether ordinary rennet, purified rennet, rennet extract, or 'rennet flower' (*Cynara cardunculus*) is used to curdle the milk.

Butter from Sheep's Milk.—The only practical method of obtaining the cream for churning is by the use of a separator. A Laval Baby separator was used by the author, the rate of running being 50 litres an hour. A sample of milk of density 1·035, containing 10·25 per cent. of fat, gave a skim-milk of density 1·047, containing 0·40 per cent. of fat, 96 per cent. of the fat being removed. In churning it is necessary to work at a temperature below 10° C., or a satisfactory consistency will not be obtained. From whey the cream may be separated as clotted cream, by setting, or by a separator; the latter is preferable.

Characters of Sheep's Butter.—The colour, unless it has been coloured, is nearly white; it has a much more greasy feeling than cow's butter, and softens at a lower temperature, though its melting-point is the same—33·5° to 35°, as against 33° to 37·7° for cow's butter. A sample contained 11·4 per cent. of water. The Reichert-Wollny figures of two samples were 27·6° and 26·5°.

Rennet.—The author finds considerable difference between ordinary rennet (obtained direct from the stomachs) and purified rennet (obtained from the former by precipitation with sodium chloride). By the use of the latter the cheese obtained was free from the peculiar odour of the sheep, which was always produced by the action of ordinary rennet, and which has always been supposed to be a characteristic of sheep's cheese. The cheese obtained by purified rennet was indistinguishable from ordinary cheese.

The remainder of the paper is devoted to the details of the preparation of various kinds of cheese, and is devoid of analytical information.

H. D. R.

On the Determination of Sand Fraudulently or Accidentally Mixed with Seeds. G. Cugini. (*Staz. Sper. Ag. Ital.*, xxiii. 568).—The author shakes 5 to 20 grammes of the seeds to be tested with chloroform in a separating cylinder, and weighs the portion which sinks to the bottom. H. D. R.

The Determination of Chromium in Ferro-Chromium. J. Spüller and S. Kalman. (*Chem. Zeit.*, 1893, xvii. 880, 881.)—Finely-powdered ferro-chromium is rapidly attacked by fusion with a mixture of three parts of caustic soda and one part of sodium peroxide (which is now an article of commerce). The chromium can be conveniently determined in the watery extract of the melt (after the decomposition of the excess of sodium peroxide) by treatment with ammonio-ferrous

sulphate and backward titration with potassium permanganate. The same fusion mixture serves for the qualitative recognition of chromium and manganese. Silver vessels should be used, as platinum is badly attacked. The use of a mixture of caustic soda and sodium peroxide is preferable to that of sodium peroxide alone, as the latter acts too violently on oxidisable alloys, such as ferro-chromium, ferro-silicon, etc. B. B.

Note by Abstractor.—The authors give no prescription for getting rid of the excess of sodium peroxide previous to the volumetric estimation of the chromium present as chromate. It could probably be effected by acidifying with acetic or sulphuric acid, and running in dilute potassium permanganate until a faint pink colour appeared, due to the completion of the decomposition by the permanganate of the hydrogen peroxide resulting from the action of the acid on the sodium peroxide. B. B.

The Determination of Chromium in Ferro-Chromium. J. Spüller and S. Kalman. (*Chem. Zeit.*, 1893, xvii. 1207, 1208.)—The authors find that a mixture of caustic soda and sodium peroxide is a good flux for ferrochromium and similar refractory substances. (See preceding Abstract.) Their experiments, which were carried out with two samples of ferrochromium nominally containing 40 per cent. and 60 per cent. of chromium respectively, led them to adopt the following method. 0·35 grms. of the very finely divided alloy is fused in a silver dish with 4 grms. of pure powdered sodium peroxide and 8 grms. of pure powdered caustic soda, the ore and flux being intimately mixed with a silver spatula, and the heating conducted cautiously over a smoky flame.* During the first five minutes the edge of the charge begins to fuse, and fusion of the whole is complete after a further period of ten minutes. Heating is continued for an hour, during the last quarter of which the melt is stirred with a silver spatula. Sudden heating at the beginning is not advisable. The basin is allowed to cool to 40-50° C., and placed bodily in hot water and the melt extracted. The basin appears to be considerably attacked, as the average loss for each time of using was 4 to 5 centigrammes on a dish weighing 38 grms. The watery solution of the melt is yellow or red-brown when the sample is poor in manganese, and it contains sodium ferrate as well as chromate. When manganese is present in considerable quantity, the solution is blue or green, from the coloration due to sodium manganate. Only traces of sodium peroxide can usually be recognised in the aqueous solution, as it decomposes when treated with hot water, especially in the presence of sodium ferrate and manganate. This property is taken advantage of to reduce these substances without reducing the chromate. 0·3 to 0·6 grm. of sodium peroxide is added little by little to the solution of the melt, until its colour appears pure yellow, from the presence of sodium chromate only. The excess of sodium peroxide is best destroyed by passing CO_2 into the hot solution for an hour, and continuing the heating for another quarter of an hour. (The author recommends the use of a bath of graphite instead of a sand bath, presumably on account of its higher conductivity.) By this process the caustic

* The smokiness of the flame cannot be essential, as the melt is an oxidising one ; an argand burner turned fairly low would probably prove suitable.—B. B.

soda and sodium peroxide are converted into sodium carbonate with the liberation of hydrogen peroxide from the latter; the hydrogen peroxide, being unstable in alkaline solution, is dissipated on heating, and the only highly-oxidised substance remaining is sodium chromate.

The aqueous solution of the melt, after having been thus purified, is transferred to a 500 c.c. flask without previous filtration, made up to the mark and a portion filtered from the ferric oxide, manganese dioxide, and alumina that remain as insoluble matter. 100 c.c. of the filtrate is used for the determination of chromium by Schwarz's method. The measured quantity is diluted with a litre of cold boiled distilled water, and acidulated with 20 c.c. of sulphuric acid containing 1 part by volume of H_2SO_4 to 5 parts of water; 100 c.c. of a solution of ammonio-ferrous sulphate containing 14 grms. of the salt per litre are added, with constant stirring, and the residual ferrous iron titrated with permanganate solution of such strength that 1 c.c. = 0·00423 grms. Fec. The strength of the ammonio-ferrous sulphate is then determined by diluting it with water as in the actual determination of chromium acidulating and titrating with permanganate to the same intensity of colour as before.

A gravimetric process, in which the same flux is used, is also described. The alloy is attacked precisely as previously detailed; the melt extracted with water, and freed from sodium ferrate and manganate and excess of sodium peroxide by the methods already laid down. The insoluble matter is then filtered, and washed with a solution of sodium carbonate to prevent its passing through the filter. The filtrate contains sodium silicate and aluminate as well as chromate, and is, therefore, taken down to dryness after the addition of 1·5 grms. of ammonium nitrate, and the residue dissolved and filtered. The filtrate is acidulated with hydrochloric acid, heated on the graphite bath, and the chromic acid reduced by 1 gramme of pure potassium nitrite. The resulting solution containing chromium as chromic oxide is precipitated hot with ammonia, avoiding an excess. After long standing at 90° C., the precipitate is filtered off, washed until chlorides cannot be detected in the washings, dried and ignited, together with the filter-paper, in a platinum crucible. A little chromium chromate is left with the silica and alumina in the residue after the evaporation with ammonium nitrate. The residue is, therefore, treated with hot dilute hydrochloric acid, whereby all the chromium and the alumina are dissolved. The solution is precipitated with dilute ammonia, and the precipitate filtered, washed, ignited, and fused with caustic soda and sodium peroxide as before, and the alumina and chromium separated by evaporation with ammonium nitrate in the manner detailed above. The small quantity of chromic oxide finally obtained is ignited and added to the main precipitate. This total chromic oxide is only an approximate measure of the content of chromium of the alloy, as, having been precipitated in the presence of alkaline salts, it not only contains alkalies, but some chromate due to oxidation of a portion of the chromic oxide in contact with a powerful base. It is, therefore, placed in a porcelain dish, covered with hot water, and rubbed down with a thick glass rod, the solution filtered, and the residue repeatedly washed. The filtrate, which contains alkaline chromate, is transferred to a porcelain basin, acidulated with hydrochloric acid, reduced with a few drops of a solution of potassium nitrite, and

precipitated with ammonia, the chromic oxide being collected, ignited, and weighed, and its weight added to that of the main precipitate which has undergone this process of purification.

The analytical figures given are in the case of the nominal 40 per cent. ferrochromium, 43·95 and 44·0 per cent. by the volumetric method, and 44·20 per cent. by the gravimetric process; the corresponding figures for the nominal 60 per cent. alloy are 57·60 to 57·68 per cent. and 57·92 per cent. The slightly higher results of the gravimetric process are to be attributed to the difficulty of removing traces of silica and alumina from the chromic oxide.

The reliability of the method of fusion was investigated by examining the insoluble matter for residual chromium; none was found.

The mixture of caustic soda and sodium peroxide can be advantageously used for many analytical purposes, where at present a mixture of sodium carbonate or caustic soda and potassium nitrate or chlorate is commonly employed. The powerful oxidizing properties of sodium peroxide, and the ease with which an excess may be removed, make it a valuable reagent. Iron pyrites can be oxidized in the same manner as ferrochromium, and the determination of sulphur affected without evaporation to get rid of nitric acid, as in the case where a mixture of sodium carbonate and potassium nitrate is used as a flux. Two samples of chrome iron ore, one containing much magnesia from Greece, the other a pure specimen from Bosnia, were completely opened up in 1¼ hours. Commercial chromic oxide, so-called "chrome-green," can be completely attacked in three quarters of an hour, and apparently the process should be applicable to the determination of chromium in chromium steel. The authors are engaged in investigating this point. B. B.

The Determination of Boron. H. Moissan. (*Compt. Rend.*, 1893, cxvi. 1087, through *Chem. Zeit.*)—Gooch's method, which consists in the volatilization of boron in the form of methyl borate, gives the best results. The author's modifications of procedure are as follows. The distilling apparatus consists of a bulb flask with a side tubulus, like that of a fractional distillation flask, but sloping first up and then down. A tap funnel is ground into the neck of the flask, and reaches down into the bulb. The flask is heated in a calcium chloride bath. The tubulus of the flask is connected with a vertical spiral condenser, and opens into a small conical flask immersed in very cold water and serving as a receiver. The connection of the end of the condenser with the receiver is made by means of a two-holed cork, the second hole being provided with a tube bent at right angles and trapped by a bulb apparatus containing ammonia (1 : 5), which catches any trace of boric acid that has escaped the spiral condenser and the cooled receiver.

In conducting an analysis the boron is first converted into boric acid, which is generally best effected by heating it with nitric acid in a sealed tube. The resulting solution, which should be of as small bulk as possible, is distilled to dryness. (In the case of an already formed borate, 1 c.c. of nitric acid is added before distillation.) The flask is then removed from the bath, 10 c.c. of methyl alcohol added, and the contents again distilled, the operation being repeated four times with fresh portions

of methyl alcohol; 1 c.c. of water and 1 c.c. of acid are then added, and distillation again carried out, three further treatments with methyl alcohol being requisite. The complete volatilization of the boron is proved by allowing a drop of the last distillate to fall on a strip of paper, which is then burnt, and the characteristic green colour due to boric acid looked for. Should any boric acid be detected, further distillation is requisite. The use of a calcium chloride bath in the distillation is to heat the walls of the flask to a temperature above the boiling-point of methyl alcohol, and thus avoid bumping. The contents of the receiver and bulb tube are emptied into a platinum crucible containing pure slaked lime which has been previously weighed as caustic lime, the crucible being meanwhile surrounded with ice-water to moderate the reaction should much acid be present. After the lapse of a quarter of an hour to allow of the completion of the reaction, the contents of the crucible is tested to make certain that it is alkaline, evaporated on the water-bath at about 70° C. to dryness, and the temperature gradually raised, ignition being completed over the blowpipe first with the crucible covered, then open. It is allowed to cool in a desiccator over caustic lime, is weighed and reheated until its weight is constant. The gain of weight is the B_2O_3 obtained. The requisite lime is prepared in the crucible in which it is to be used. Calcium nitrate is ignited until it is partially decomposed, in which state it can be conveniently stored. When needed a portion is ignited to constant weight, and used as described above. For the retention of 0·5 grm. of B_2O_3, 8 to 10 grms. of lime are requisite. The method, when carefully performed, is accurate and generally applicable. B. B.

Note by Abstractor.—It is futile to attempt to render '8 to 10 grms.' of lime completely caustic over any ordinary blowpipe. The use of a muffle is indispensable. B. B.

Titration of Alkaline Liquids Containing Hypochlorite. C. Ullmann. (*Chem. Zeit.*, 1893, xvii. 1207, 1208.)—It is frequently necessary in examining liquids that have been subjected to electrolysis to determine their alkalinity when chlorine and hypochlorites are present. For example, when a solution of sodium chloride, which has been electrolyzed, and contains (in addition to undecomposed sodium chloride) sodium hydrate, sodium hypochlorite, and possibly sodium chlorate, is to be tested, the usual methods are not available. Ordinary indicators are destroyed, and such acids as hydrochloric, nitric, sulphuric and oxalic are inapplicable. The author has found succinic acid to be of service and uses it in the following manner. A measured quantity of the liquid to be examined is heated with an excess of a standard solution of succinic acid until the smell of hypochlorous acid is no longer recognised. Phenol-phthalein is then added, and the solution titrated back with caustic soda. The utility of the succinic acid results from the facts that it is not volatile, that it decomposes carbonates and hypochlorites, but not chlorides, and that it is not affected by the oxidising and chlorinating action of the electrolyzed salt solution. B. B.

Quantitative Precipitation in Presence of Hydroxylamine. P. Jannasch and J. Mai. (*Berichte*, 1893, xxvi. 1786.)—As an example of this application of

hydroxylamine the authors quote the following method for precipitating chromium hydroxide from bichromate. About one gramme of potassium bichromate is dissolved in 50 c.c. of water and heated with 10 c.c. of concentrated hydrochloric acid and 25-30 c.c. of alcohol, until the liquid is green and the greater part of the excess of alcohol has been expelled. The solution is diluted to 300 c.c., and heated; 2 grammes of pure hydroxylamine hydrochloride are added and the chromium precipitated by a considerable excess of ammonia. The violet-red coloured precipitate is immediately filtered through two filters, washed with boiling water, and dried sufficiently to enable the filter to be transferred to a platinum crucible, where it is ignited. The excess of ammonia used has no solvent action on the precipitate, which filters more readily, is more easily washed, and is less liable to contain silica than is the precipitate with ammonia obtained in the usual way. A. G. B.

A New Method for the Determination of Yellow Phosphorus. J. Toth. (*Chem. Zeit.*, 1893, xvii. 1244, 1245.)—The following method has been devised for the determination of yellow phosphorus in mixtures containing phosphoric acid as a product of oxidation of the element. The principle underlying it consists of the extraction of the phosphorus with CS_2, precipitation of the dissolved phosphorus as silver phosphide, oxidation of the latter with nitric acid and determination of the resulting phosphoric acid in any convenient way.

The accuracy of the process thus outlined was ascertained as follows: A small piece of yellow phosphorus was cut out of the centre of a stick, quickly immersed in alcohol, then in ether, and finally in a vessel containing olive-oil, which had been proved to yield no phosphoric acid when shaken with nitric acid. The olive-oil, together with the vessel containing it, was weighed before and after the introduction of the phosphorus, and thus the weight of the latter ascertained. CS_2, which had been proved free from H_2S by its remaining colourless when shaken with silver nitrate solution, was then added, dissolving the phosphorus, and the resulting solution was diluted with a large quantity of olive-oil, so that each gramme of oil contained 1-2 mgrm. of P. Weighed portions of the oil were taken to test the method of estimation. For example, 20 grammes of the oil were shaken with 10 c.c. of a 5 per cent. solution of silver nitrate, and 10 c.c. of water in a flask of 200-300 c.c. capacity until the separation of silver phosphide was complete. 20 c.c. of dilute nitric acid were then added, and the mixture warmed on the water-bath, and shaken until the oil-layer became bright brown, when the removal of silver phosphide was complete. The oil was separated by filtration through a wet filter and washed; the filtrate boiled for ten minutes, cooled and precipitated with molybdic solution, the phosphorus being ultimately weighed as $Mg_2P_2O_7$. When a small quantity of phosphorus, *e.g.*, 7 mgrs., was used the result was low (78 per cent. of the theoretical). Better results were obtained when working on 15-35·6 mgrs., viz. 93 to 100 per cent.

The process having proved reasonably exact, considering the nature of the case, can be used for the determination of phosphorus in sundry confections used medicinally. The preparations (*e.g.*, chocolate bonbons) are rubbed down with CS_2 in a porcelain mortar, filtered and re-treated until the filtrate gives only a slight brown coloration when shaken with silver nitrate. Oxidation must be hindered as far as

possible by covering the funnel with a clock glass. Silver nitrate solution is shaken with the extract, dilute nitric acid then added, and the CS_2 distilled off. The remainder of the process is carried out as described above. B. B.

The Solubility of Difficultly Soluble Salts. A. F. Holleman. (*Zeits. physik. Chem.*, 1893, xii. 125; through *Chem. Zeit.*)—The author has determined the solubility of salts generally termed insoluble by estimating the electrical conductivity of their saturated solutions, which should, according to the dissociation theory of solution of Van't Hoff, contain free ions only, to the number of which the electrical conductivity is proportional. The following are the results obtained.

Salt.	Parts of water for solution of one part of salt.	Temperature. ° C.
$BaSO_4$ ...	429,700 ...	18·9
,, ...	320,000 ...	37·7
$SrSO_4$ ...	10,070 ...	16·1
,, ...	10,030 ...	26·1
AgCl ...	715,800 ...	13·8
,, ...	384,100 ...	26·5
AgBr ...	1,971,650 ...	20·2
,, ...	775,400 ...	38·4
AgI ...	1,074,040 ...	28·4
,, ...	420,260 ...	40·4
CaC_2O_4 (? 2 H_2O) ...	148,220 ...	13·6
,, ...	124,400 ...	24·6
$BaCO_3$ ...	64,070 ...	8·8
,, ...	45,566 ...	24·2
$SrCO_3$ ...	121,760 ...	8·8
,, ...	91,468 ...	24·3
$CaCO_3$ ...	99,500 ...	8·7
,, ...	80,040 ...	23·8

B. B.

The Use of Definite Voltages for Electrolytic Separations. H. Frendenberg. (*Zeits. physik. Chem.*, 1893, xii. 97; through *Chem. Zeit.*)—The author has extended recent work dealing with the electrolytic separation of metals by the use of currents of definite pressures. He classifies metals into three groups: (1) Those which are not separable from their aqueous solutions by currents of moderate voltage, *e.g.*, the metals of the alkalies and alkaline earths — aluminium and chromium; (2) Those which can be precipitated on the anode as peroxides, viz., lead manganese and thallium; (3) Those appearing in the metallic state on the cathode. The voltage of the current has but little influence on the separation of these three groups, but applies chiefly to the separation of members of the third group. The author uses a Gülcher thermo-electric battery because the Daniell, Leclanché, and Meidinger cells give currents of low voltage, and that of the Bunsen is too variable for the purpose in hand, which necessitates an approximately constant electrical pressure. As the voltage, and not the total electrical energy, is to be measured, the use of the oxyhydrogen voltameter, is abandoned in favour of a suitable galvanometer. The separation of various metals was effected, precipitation being conducted in platinum dishes. Thus silver was separated from copper in a mixed solution of

their nitrates—acid with nitric acid—by a current having a pressure of 1·3 volt. Silver was also separated from bismuth from a solution of the nitrates—acid with nitric acid—by a current of the same voltage. Silver was separated from arsenic (1·7 to 1·8 volt), and from antimony (1·2 to 1·3 volt), and from cadmium (1·6 volt). Similar separations were effected for silver from platinum and zinc; mercury from copper, bismuth, arsenic, antimony, and cadmium; and for copper from many other metals. In most solutions the voltage requisite to precipitate copper is 1·8 volt, but in an oxalic solution 1·1 volt suffices. Copper was separated from cadmium and arsenic, and in the case of the latter metal, both in sulphuric acid solution at 1·85 volt, and in nitric acid solution at 1·9 volt. B. B.

Recovered Rubber. R. Henriques. (*Chem. Zeit.*, 1893, xvii. 1266.)—The importance of the American trade in recovered rubber may be gathered from the fact that about twenty-five million pounds of old overshoes are collected and worked up annually. Two processes of recovery are in use. According to the first, the rubber is finely ground, sifted to separate it from fragments of textile material, steamed under a pressure of six atmospheres, and rolled into plates. In the second method the raw material is divided into pieces about 1 sq. cm. in size by passage between channelled rollers, boiled with dilute sulphuric acid to remove textile materials, washed with water alkaline with soda, finely ground and steamed in the same manner as in the former case. Apparently the steaming process partly devulcanizes the rubber, as otherwise it could scarcely be moulded. This view is upheld by the observation that recovered rubber only contains a little vulcanizing sulphur, but a good deal of sulphuric acid (presumably as sulphates).

Analyses are given of three samples of rubber put upon the market by the Rubber Reclaiming Company, New York, in the form of black rolled plates 3-5 mm. in thickness, possessed of no great elasticity, and, in fact, resembling ordinary black rubber goods of common quality. The material is loaded with mineral matter, as is common for goods of this class, the following figures being obtained:

	A.	B.	C.
Sp.Gr.	1·66	1·59	1·65
PbO	12·87	14·02	12·23
$CaSO_4$	22·13	21·59	21·43
$CaCO_3$	18·00	10·91	17·86
$Fe_2O_3 + Al_2O_3$	0·80	2·74	1·10
SiO_2	1·75	0·40	1·60
H_2O	0.52	0·55	0·62
Vulcanizing S	0·71	2·03	1·40

Fatty oils and rubber surrogates were looked for by the author's new methods (ANALYST, xviii., 223), but were absent. Asphalt and lampblack were recognised qualitatively, but no exact process for their estimation yet exists.

But little information has been published as to the composition of rubber used for such purposes as the manufacture of overshoes. One recipe which has appeared gives 18 parts of Para rubber, 11 of litharge, 40 of chalk, 3 of asphalt, ½ of lampblack, and 11½ of sulphur. The product would be brittle, however, on account of the small percentage of rubber and the large proportion of sulphur. In other

respects it will be seen to be similar to the mixtures sold as recovered rubber, the composition of which is given above. In this recovered rubber it is a matter of much difficulty to determine with precision the content of true rubber, but it may be taken as in no case higher than 35 to 40 per cent. B. B.

New Volumetric Methods for the Valuation of Fowler's Solution and of Tartar Emetic. S. Györy. (*Zeit. Anal. Chem.*, 1893, xxxii. 415; through *Chem. Zeit.*)—Five c.c. of Fowler's solution (*Liq. Arsenicalis*) are diluted with 10 c.c. of water; 0·5 to 1 gramme of potassium bromide is added, and the whole acidified with 10 per cent. hyrochloric acid; a drop of methyl-orange solution (1 : 1000) is added, and the solution titrated with $\frac{N}{10}$ potassium bromate solution until the red colour disappears. The addition of a drop too much of the potassium bromate solution will be revealed by the yellow colour of the bromine. For the similar treatment of tartar emetic 0·3 gramme is taken, and 25 c.c. of 10 per cent. hydrochloric acid are added. A simplification of the process may be effected by pretermitting the addition of potassium bromide; for the oxidation of arsenious or antimonious oxide by potassium bromate in presence of hydrochloric acid must yield hydrobromic acid, which will be ready to react with evolution of bromine when an excess of potassium bromate has been added. A. G. B.

Separation of Arsenic from Antimony. L. Garnier. (*Jour. Pharm. Chim.*, 1893, [5], xxviii. 97; through *Chem. Zeit.*)—Dragendorf's method for separating these two metals in toxicological analysis consists in treating the mixed sulphides with ammonia, fusing the undissolved antimony sulphide, still containing some arsenious sulphide, with sodium nitrate, and dissolving any sodium arsenate which may have been formed with water, in which the sodium antimoniate is practically insoluble. The author finds that ammonia always dissolves some antimony sulphide, together with the arsenious sulphide; he therefore recommends Ritter's method. This is performed by dissolving the mirror of arsenic and antimony obtained by Marsh's process in aqua regia and treating the solution with a mixture of tartaric acid, magnesium sulphate, ammonium chloride, and excess of ammonia. The arsenic is precipitated as ammonium magnesium arsenate, and the antimony is thrown down in the filtrate by hydrogen sulphide. A. G. B.

EXTRACT FROM THE REPORT OF THE COMMISSIONERS OF THE INLAND REVENUE.

The following is taken from the report of the Principal of the Somerset House Laboratory:

The systematic examination into the composition of genuine milk alluded to in my last report has been continued during the year, and the results show that while there has been a sensible improvement as compared with the results obtained in previous investigations in the quality of milk as regards the proportion of fat, the percentages of non-fatty solids in the several milks were relatively in agreement with the figures formerly obtained; whatever difference exists is in the direction of a somewhat larger proportion of the milks giving non-fatty solids in amount under 8·6 per cent. It is

now, therefore, more than ever apparent that a limit of 8·5 per cent. for determining the presence of added water, when judging from the non-fatty solids only, is as high as can be fairly justified, not only in respect to milk from single cows, but also in the case of verified mixed dairy samples.

The results afforded by this investigation, which embrace the milk of 273 individual cows, and the mixed milk of 55 dairies, have been forwarded to the Local Government Board for publication in their annual report.

REFERENCES UNDER THE "SALE OF FOOD AND DRUGS" ACTS.

Fifty-one samples have been referred to us by the magistrates under these Acts. They comprised milk, butter, lard, coffee, whisky, laudanum, pepper, and mineral waters.

Thirty-seven of the samples, or three-fourths of the whole number, consisted of milk. The charge in 24 of the samples was for dilution with water; in eight for abstraction of fat; and in five both offences were alleged to have been committed. Of the samples alleged to contain added water, our results enabled us to support the charge in 22 out of the 24 cases; and of those, where fat was alleged to have been abstracted, we were able to report in a similar way in seven out of the eight cases. Of the five samples where both offences had been charged, we agreed fully with the Public Analyst in four of the cases, but only as regarded added water in the fifth. We could not concur in this case as to the second charge of abstraction of fat, as the sample had been purchased and was labelled as "skim milk," and as it contained much more fat than "skim milk" usually does, we reported that, while the sample undoubtedly contained added water, it could only be considered as deficient in fat when compared with whole milk.

Of five samples of butter, two were alleged to contain foreign fat, and one excess of water; as to the other two we are not aware what offence was charged. The last-named two samples corresponded in composition with genuine butter, as also did one of the samples alleged to contain foreign fat. In the other sample alleged to contain foreign fat, as well as in that where excess of water was charged, we concurred in the conclusions of the Public Analyst.

In two samples of lard, one of whisky, one of laudanum, and one of pepper, we agreed with the public analyst.

In one sample of coffee alleged to contain 94 per cent. of chicory, it was contended on the part of the defendant, who had had the coffee examined by another analyst, that the percentage of chicory was very largely overstated, and this we found to be the case.

In three samples of mineral water, alleged to contain lead, we found that while lead was present, the quantity was extremely minute, and that the metallic contamination was principally tin.

CORRESPONDENCE.

To the Editors of the ANALYST.

GENTLEMEN,—In reference to the criticisms by Messrs. Richmond and Boseley in your last number, on our method of titrating mixtures of milk-sugar and cane-sugar, kindly allow us a few words of explanation.

We do not object to criticism of the method; what we do object to is the failure of these two gentlemen to see that the fluid recommended by us (ANALYST, x. 62) contained caustic soda and Rochelle salt, while the fluid they still contend as invalidating our results contained neither of these (ANALYST, vi. 218).

We are now content to leave the method to those who care to try it.—Yours faithfully,

ALF. W. STOKES.
R. BODMER.